

**STUDY OF CONDITIONS FOR CONDENSATION AND DESORPTION OF PCDD
ON PARTICULATE MATTER UNDER STACK SAMPLING CONDITIONS**

FINAL REPORT OF PROJECT 129

ONTARIO MINISTRY OF THE ENVIRONMENT

UNIVERSITY OF WATERLOO

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STUDY OF CONDITIONS FOR CONDENSATION AND DESORPTION OF PCDD
ON PARTICULATE MATTER UNDER STACK SAMPLING CONDITIONS

Final Report of Project 129

To: The Ontario Ministry of the Environment

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Summary

In stack sampling of flyash particulates the adsorption/desorption behaviour of polychlorinated dibenzo-p-dioxins (PCDD) at the gas/solid interface between the flyash surface and the stack gases is an important but unknown phenomenon that must be considered for obtaining accurate analytical results. Some aspects of the desorption and adsorption behaviour of PCDD on flyash particulates were investigated in this work. PCDD were found to desorb from flyash particulates at temperatures below 200°C. A small percentage of the PCDD, about 10 percent, could not be desorbed and are thought to be chemisorbed on the surface of the flyash particles. PCDD survived desorption undecomposed and were trapped on clean flyash downstream of the heated sample.

Further studies are needed to investigate the range of variables specific to stack sampling conditions. With improvements in experimental design more precise determination of desorption rates for each congener class can be obtained. Only limited adsorption data were obtained in this study for flyash particulates. None were obtained for the fluorisil adsorbant used in the stack sampling train. Since these phenomena are an important aspect of stack sampling, accurate data are needed. Also, selected experimental data needs to be obtained for air rather than nitrogen.

These physical-chemical data were obtained by analytical chemical methods using GC/MS/Computer instrumentation. These data could not be obtained in such a complex sample without the application of the powerful data acquisition and data reduction capabilities of these computerized instruments. These data provide fundamental information that can be used to understand the mechanism of PCDD and PCDF formation on the particulates.

CONCLUSIONS

There were few qualitative changes in the organic content of the flyash due to heating.

A minimum of 70 percent of the PCDD were desorbed after heating for 16 hours at temperatures between 100 and 200°C.

At least 10 percent of the PCDD could not be desorbed under maximum time and temperature conditions and are thought to be chemisorbed on the surface of the flyash particles.

Heating the flyash at 120°C under a 100 mL/min stream of N₂ desorbed 15 to 38 percent of the PCDD.

The desorption rates for the PCDD congeners were estimated to be 0.037, 0.086, 0.15, 0.23, ng/g/hr/L for TCDD, P₅CDD, H₆CDD and H₇CDD respectively. At constant temperature these rates appear to depend mainly upon the amount of material originally present on the flyash, not on physiochemical properties such as vapour pressure or dipole moment.

When expressed as percent/hour, desorption rates for the PCDD congeners are equal. The average value is 0.78 percent/hr/L.

Desorbed PCDD were absorbed on clean trap flyash downstream with no apparent decomposition.

The apparatus and data were inadequate to permit determination of adsorption rates.

Introduction

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are groups of compounds which are among the most toxic. Since 1977 it has been known that PCDD are produced as a by-product of municipal garbage incineration (1-6). Sampling of stack gases from incinerators has shown that PCDD are emitted into the atmosphere (7). As a result, the Ontario Ministry of the Environment has set guidelines for PCDD emissions from incinerators.

For many years in the United States and Canada the EPA Method 5 Sampling Train has been used to monitor the gaseous and particulate emissions of incinerators (8). However, much is not known about the fate of some compounds in the train. In the sample train a glass fiber filter to trap particulates is placed upstream of impingers and adsorbant cartridges. This filter is maintained at 120°C for a minimum sampling time of four hours. Because of unknown behaviour of adsorption and desorption of organic compounds on the trapped particulates it is not known whether the relative amounts of PCDD found on the filter and in the impingers is truly indicative of the relative amounts in the stack effluent. Sampling artifacts could be introduced by adsorption or desorption of PCDD on the particulate matter on the filter. It is important to know the true distribution between gas and particles as gaseous state PCDD are a possible health hazard. Also, this information will aid in understanding the mechanism of formation of PCDD during incineration.

Therefore the purpose of this study was to investigate adsorption and desorption behaviour of PCDD on flash particles. This report presents the results and recommendations for further studies into this problem.

Materials and Methods

Materials

Flyash from the Commissioner Street incinerator was supplied by the Ontario Ministry of the Environment. All solvents were "distilled in glass" UV grade (Caledon Laboratories, Toronto, Ont., Canada). Unlabelled PCDD standards were purchased from Ultra Scientific Inc. (Hope, R.I., U.S.A.) and Cambridge Isotopes (Woburn, MA., U.S.A.). Labelled PCDD standards, [$^{13}\text{C}_{12}$]TCDD and [$^{13}\text{C}_{12}$]OCDD were supplied by the Ontario Ministry of the Environment.

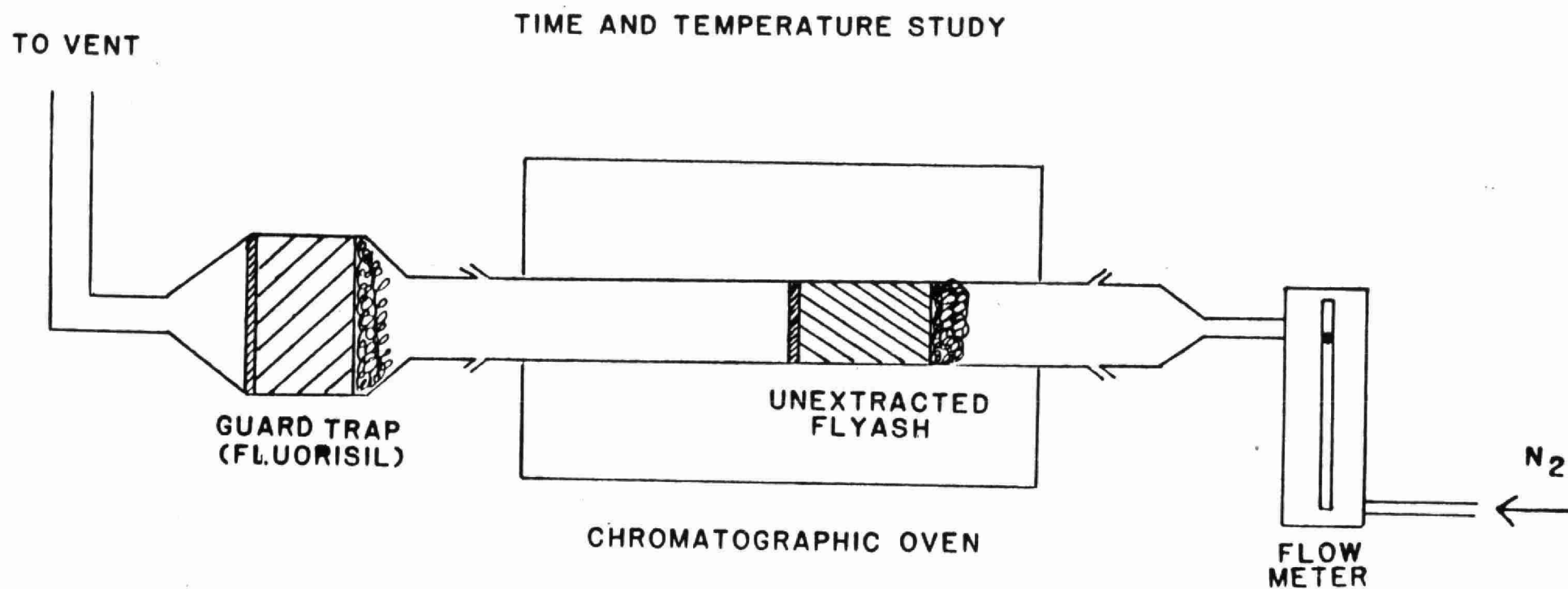
Pyrex tubes 45 cm x 2 cm I.D. were constructed with a medium porosity glass frit.

All glassware was washed in an ultrasonic bath for approximately thirty minutes using a mild detergent. Following rinsing with deionized water, glassware was dried overnight in an oven at 275°C. Before use glassware was rinsed with benzene. Soxhlet extraction apparatus was rinsed by refluxing benzene for two hours. The rinse benzene was discarded and fresh benzene used for the flyash extraction.

Time and Temperature Studies

The experimental apparatus is shown in Figure 1. About 15 g of flyash was placed in the Pyrex tube on the upstream side of a glass frit. A plug of clean glasswool was used to retain the flyash. The tube and contents were placed in a modified gas chromatograph oven. A fluorisil trap was attached to the downstream end of the tube outside the oven to trap desorbed material. The flyash was heated under a flow of 100 mL/min. high purity dry nitrogen at temperatures of 100, 150 and 200°C. At each temperature the flyash was heated for 16, 32 and 48 hours.

FIGURE 1 APPARATUS FOR DESORPTION OF PCDD FROM FLYASH



Time Studies at Constant Temperature

The apparatus is shown in Figure 2. Flyash was sieved and the 170-200 Mesh fraction was used for these experiments. About 15 g of the unextracted flyash was placed in the Pyrex tube on the upstream side of the glass frit. About 12 g of exhaustively extracted flyash was placed downstream of the unextracted flyash against the glass frit. Flyash was retained with glasswool plugs. The tube and contents were heated at 120°C for 2, 4, and 6 hours in duplicate under a 100 mL/min flow of high purity nitrogen. Any desorbed organic compounds not absorbed by the trap flyash were absorbed by a fluorisil guard trap. A flowchart of the experiment is shown in Figure 3.

Extraction and Concentration

The flyash was transferred to a glass thimble with a medium porosity glass frit. 20 ng of [$^{13}\text{C}_{12}$]ICDD and 14 ng of [$^{13}\text{C}_{12}$]OCDD internal standards in isooctane were added to the flyash in the time studies. Organic compounds were extracted with 200 mL benzene in a Soxhlet extractor for 18 hours. The extract was reduced to several mL by rotary evaporation under reduced pressure. Final concentration to 300 μL was achieved by blowing a gentle stream of high purity nitrogen over the surface of the sample in a calibrated 1 mL reaction vial. In the event that particulate matter was suspended in the extract after rotary evaporation, the extract was transferred to a centrifuge tube and centrifuged to drive the particles to the bottom. The extract was transferred with rinsing to a pear-shaped flask and concentrated further.

Gas Chromatographic Analysis

Total organic compounds (TOC) were estimated by using gas chromatography - flame ionization detector (GC-FID) techniques. The Hewlett-Packard 5880 GC was

FIGURE 2 APPARATUS FOR DESORPTION AND ADSORPTION OF PCDD FROM FLYASH

TIME STUDY AT CONSTANT TEMPERATURE

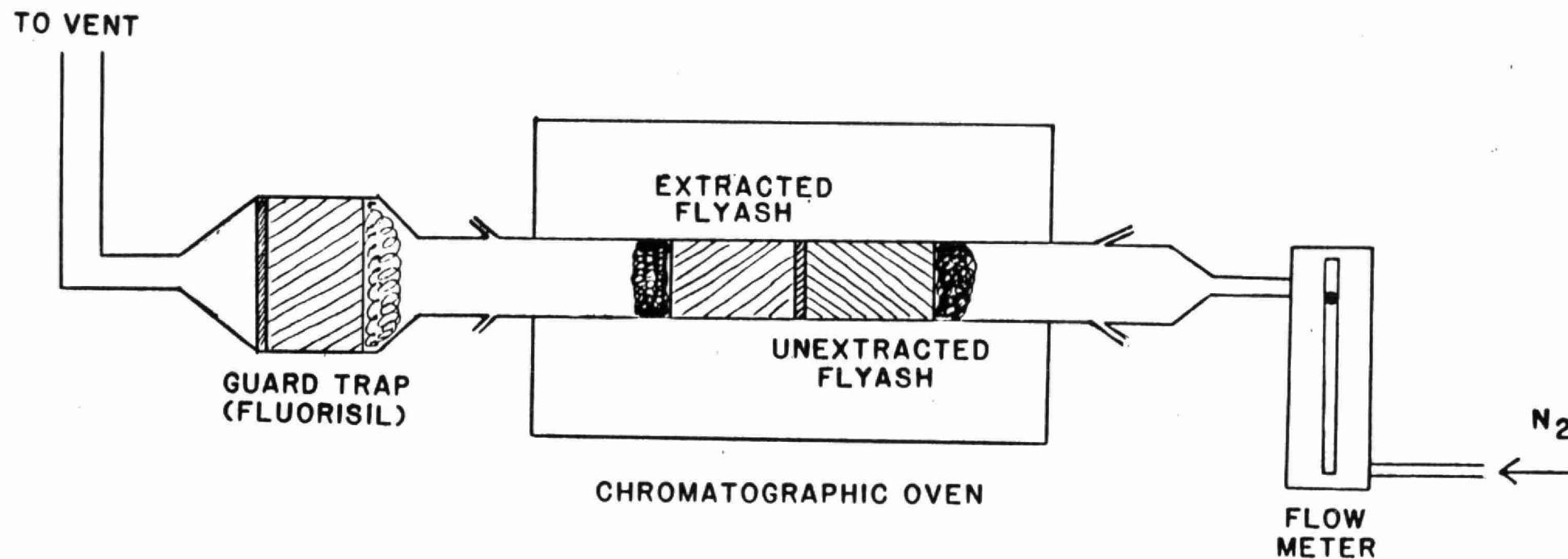
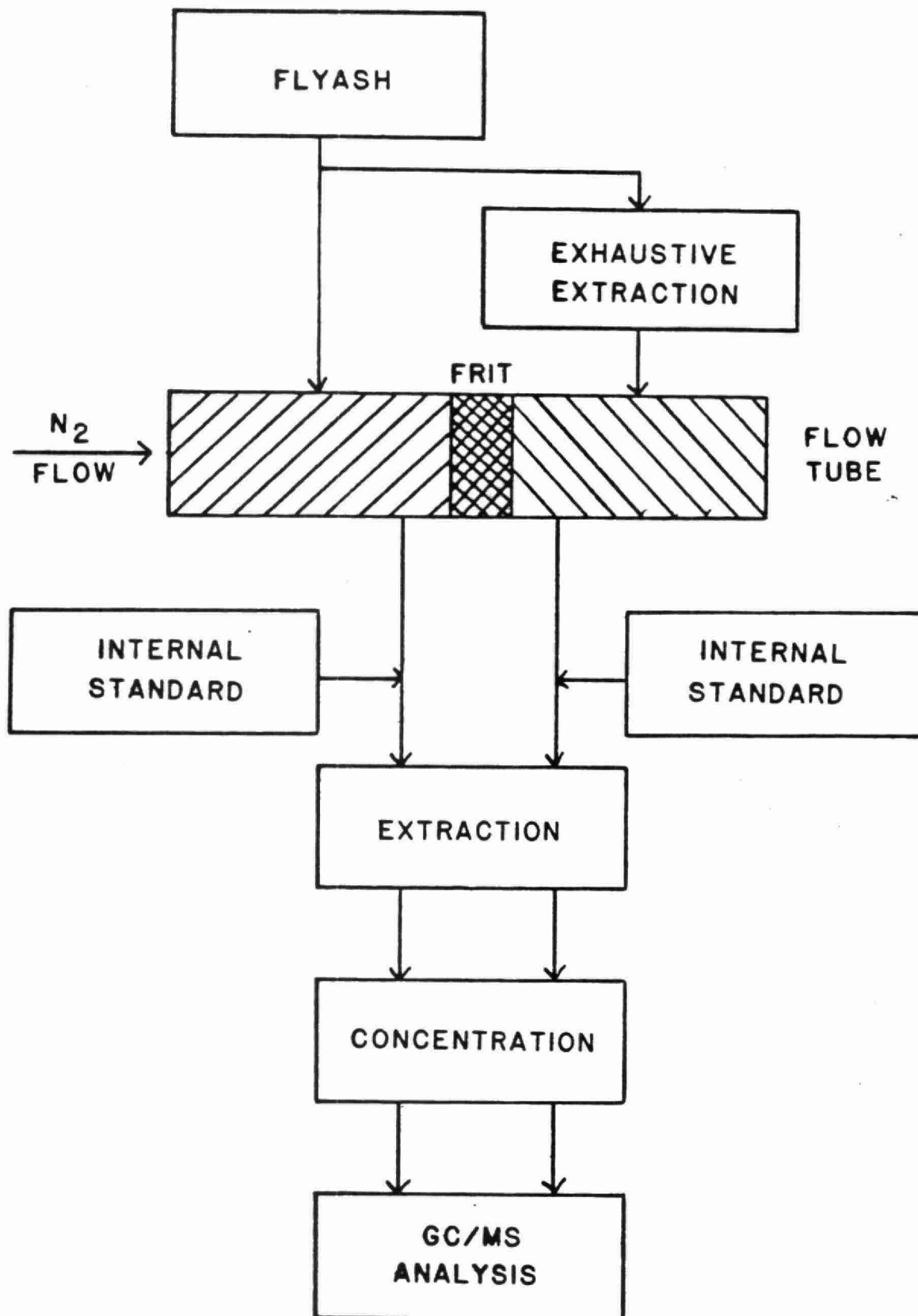


FIGURE 3 FLOWCHART OF FLYASH ANALYSIS

TIME STUDY AT CONSTANT TEMPERATURE



equipped with cool on-column injection, a fused silica WCOT column 30 m x 0.32 mm ID coated with a 0.25 μ m thick DB-5 stationary phase (J & W Scientific, Rancho Cordova, CA., U.S.A.) and a Level 4 terminal-integrator. Chromatographic conditions were: helium carrier gas flow 2.5 mL/min., temperature program 90°C to 300°C at 6°C/min. TOC were estimated using a response factor of 8 area counts/ng, based on average response factors for different compound classes (9).

Gas Chromatography/Mass Spectrometry Analysis

Analyses were carried out on a Hewlett-Packard 5987A gas chromatograph/mass spectrometer (GC/MS) with an HP1000 data system. The HP5987A GC/MS has a mass spectra search system, Probability Based Matching (PBM) and Self Training Interpretive Retrieval System (STIRS) based on over 70,000 reference spectra. The instrument was equipped with a cool on-column injector, a fused silica 30 m x 0.32 mm I.D. DB-5 column (J & W Scientific, Rancho Cordova, CA., U.S.A.) and a direct inlet GC/MS interface. Instrument operating parameters are given in Table 1.

TABLE 1: Instrument Operating Parameters

Chromatographic Conditions

Fused silica WCOT column 30 m x 0.32 mm I.D.

Stationary phase DB-5, 0.25 μ m thickness

Helium carrier gas flow 2.5 mL/min.

Temperature program 90°C to 300°C at 6°C/min.

Linear Scan Mass Spectrometry

Scan range 50 amu - 500 amu

Scan rate 630 amu/s

Selected Ion Monitoring Mass Spectrometry

<u>Ions</u>	<u>M/Z</u>	<u>dwell (ms)</u>
TCDD [M+2] ⁺	321.9	100
[¹³ C ₁₂]TCDD [M+2] ⁺	333.9	100
P ₅ CDD [M+2] ⁺	355.9	100
H ₆ CDD [M+2] ⁺	389.8	100
H ₇ CDD [M+2] ⁺	425.8	100
OCDD [M+2] ⁺	459.7	100
[¹³ C ₁₂]OCDD [M+2] ⁺	471.7	100

RESULTS AND DISCUSSION

Extraction of Organic Compounds

The precision of the extraction step was estimated by extracting the raw flyash in triplicate and determining the TOC in each extract. Two one- μ L aliquots of each extract were injected into the GC.

The TOC analyses of the flyash extracts are presented in Table 2. The response factor of 8 area counts/ng is an estimate which can vary between 4 and 14 area counts/ng, depending on the relative proportions of the different compound classes. The determination is quite reproducible (precision) but can only be considered semi-quantitative, with an error of 200 percent (accuracy). However, since the relative proportions of the compound classes are constant between replicates, the analyses can be used to determine the variance of the extraction step. Bartlett's Test of homogeneity of variances was used to determine if the three extracts were not significantly different from each other (10). Since the test indicated no difference between extractions, the pooled variance was used to determine the relative error of the extraction step, which was 4.3 percent.

Time and Temperature Study

There were few qualitative changes in the organic content of the flyash due to heating, as shown in Figure 4. The major peak at 28.2 minutes in the unheated sample was missing in the heated sample. This compound, identified by spectra library matching as molecular sulphur (S_8), likely decomposed during heating. Some of the major components detected in the undesorbed flyash were detected in the trap flyash chromatogram. The large peak at 45 minutes was identified as a phthalate ester. This likely originated by desorption with nitrogen from the Tygon tubing used to connect the gas supply to the flow meter.

TABLE 2: Total Organic Carbon in Flyash Extracts

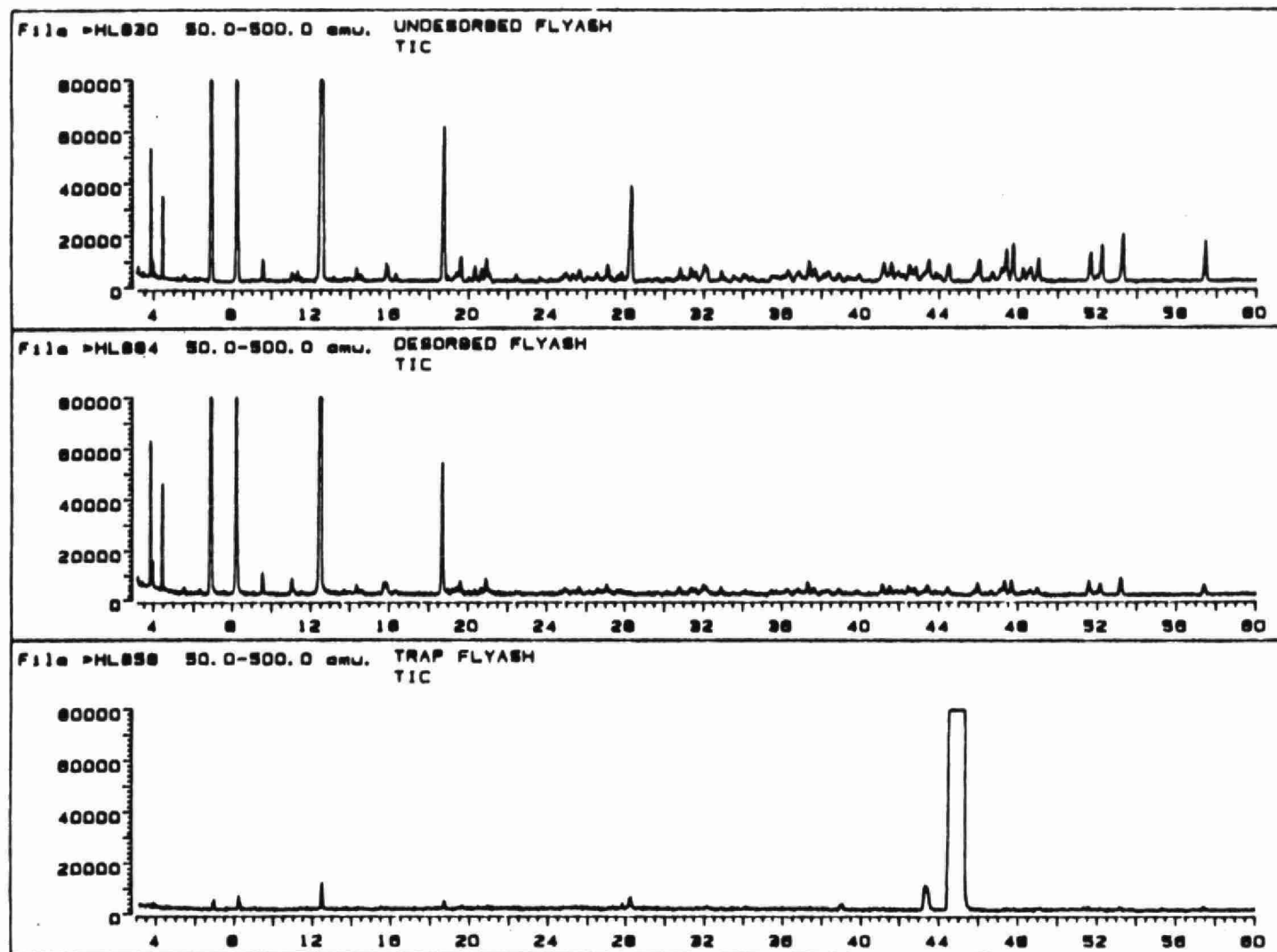
<u>Extract</u>		<u>MOE I</u>	<u>MOE II</u>	<u>MOE III</u>
Injection	1	16540 ^a	18250	16170
	2	16220	16320	17680

^a ng/g flyash

Average TOC is 17030 ng/g; pooled standard deviation (S.D.) is 738 ng/g;
relative standard deviation (R.S.D.) is 0.043.

FIGURE 4

GC-MS ANALYSIS OF FLYASH



Figures 5 through 8 show portions of selected ion chromatograms from GC-MS-SIM analyses of flyash heated for 48 hours at three temperatures. Plots A, B, and C in each figure are from desorption experiments run at 100, 150, and 200°C. Plot D in each figure is from an analysis of a standard containing PCDD standards each at a concentration of 50 ng/ μ l. The retention time scale, in minutes, is shown at the bottom of each plot. The full scale abundances of the plots are equal to the maximum abundances of the corresponding standard.

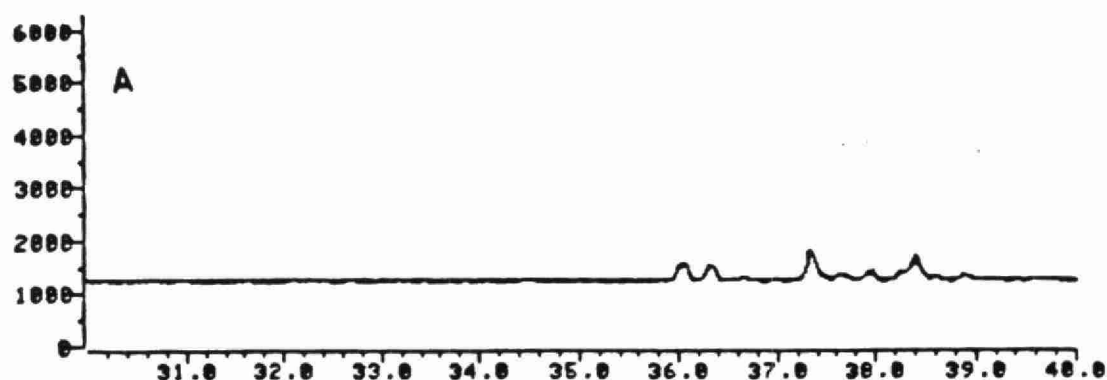
The percent loss of each PCDD congener is shown in Table 3 and presented graphically in Figure 9. The data were tested for temperature and time effects by a 2-Way Model I analysis of variance (ANOVA) without replication (10). Within each group of PCDD congeners there was no significant effect due to temperature or heating time at the ninety-five percent confidence level. The relative precision of the quantitation procedure was estimated from the ANOVA to be eight percent relative.

It had been expected that the amount of PCDD desorbed would increase with an increase in temperature with heating time held constant and would increase with an increase in heating time with temperature held constant. The high amount of material desorbed, between 68 and 89 percent, and the lack of time and temperature dependence suggests that the PCDD were desorbed in a time shorter than 16 hours. Since all the PCDD were not desorbed even after heating for 48 hours at 200°C it is possible that some of the PCDD are more tightly bound (chemisorbed) to the surface of the flyash and would not desorb under the experimental conditions. The majority is just absorbed through van der Waals forces (physisorbed). The presence of two different types of adsorption is supported by the data of Rordorf and Eiceman (11, 12). Rordorf measured the vapour pressure of

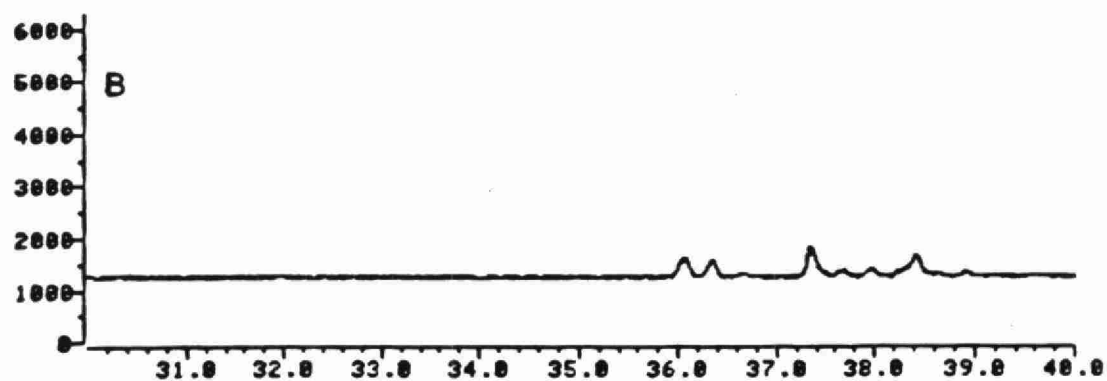
FIGURE 5 GC-MS-SIM ANALYSES FROM TIME AND TEMPERATURE STUDY

TCDD

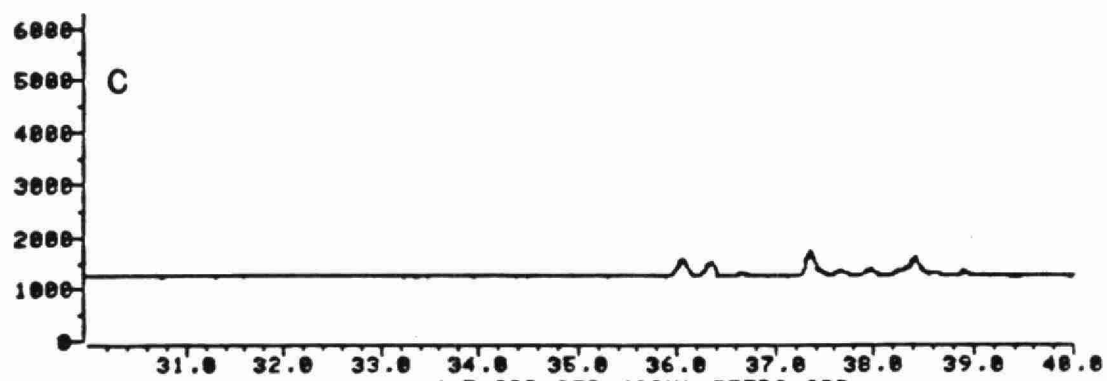
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File >LS837 321.6-322.6 amu.MOE H-150-48 (SIM) TETRA-CDD
EIP



File >HS838 321.6-322.6 amu.MOE H-200-48 (SIM) TETRA-CDD
EIP



File >LS836 321.6-322.6 amu.417-CDD STD (SIM) TETRA-CDD
EIP

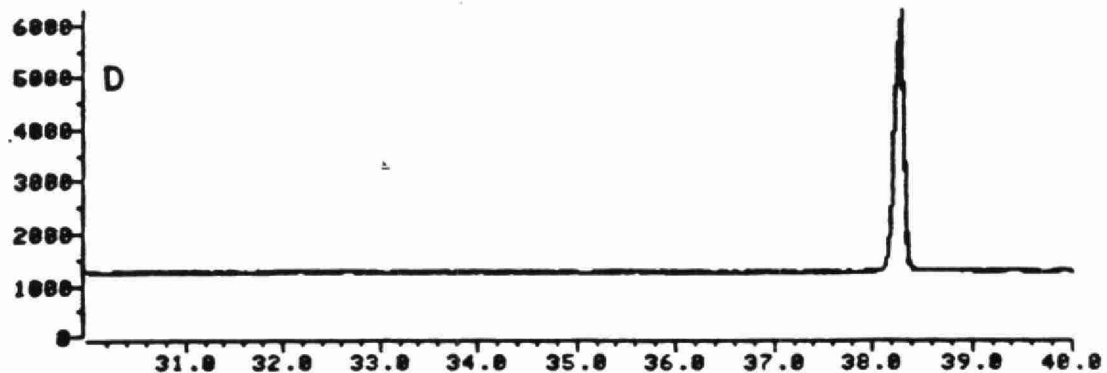
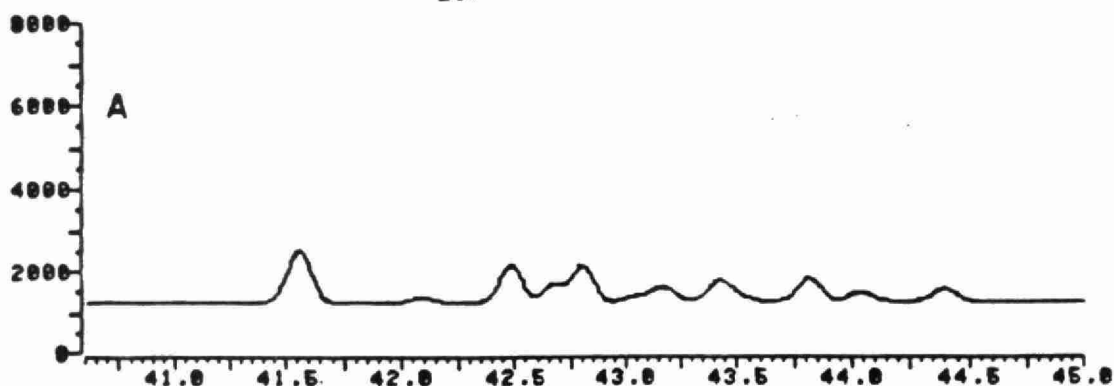
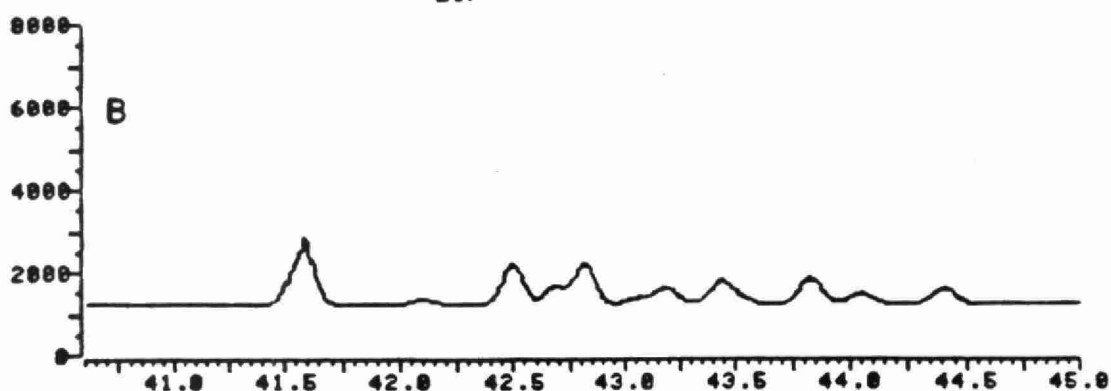


FIGURE 6 GC-MS-SIM ANALYSES FROM TIME AND TEMPERATURE STUDY
P5CDD

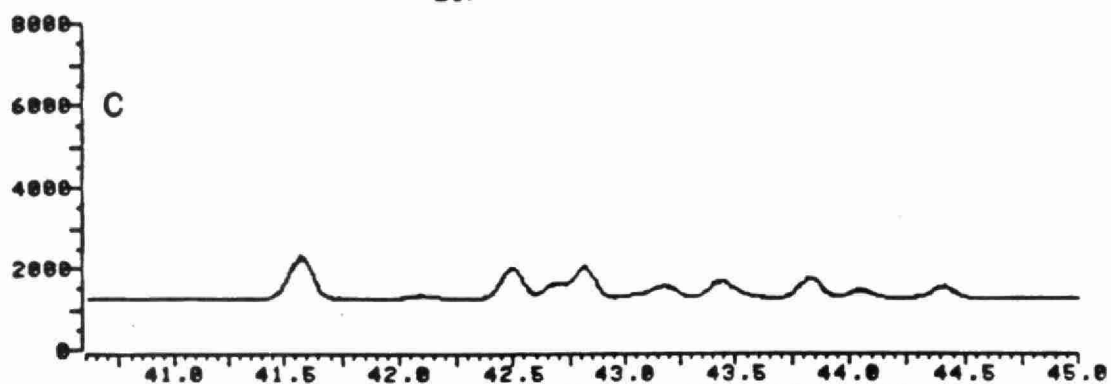
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EIP



File >LS837 355.6-356.6 amu.MOE H-150-48 (SIM) PENTA-CDD
EIP



File >HS838 355.6-356.6 amu.MOE H-200-48 (SIM) PENTA-CDD
EIP



File >LS836 355.6-356.6 amu.MOE 4:7-CDD STD (SIM) PENTA-CDD
EIP

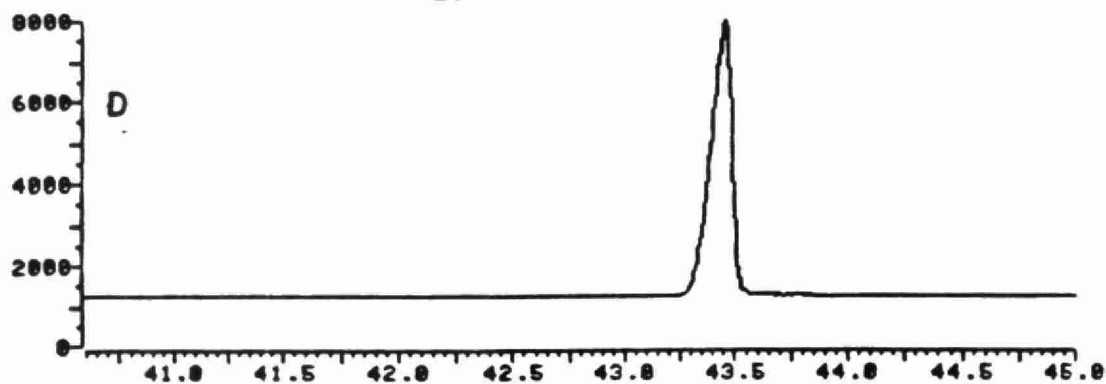


FIGURE 7 GC-MS-SIM ANALYSES FROM TIME AND TEMPERATURE STUDY
H6CDD

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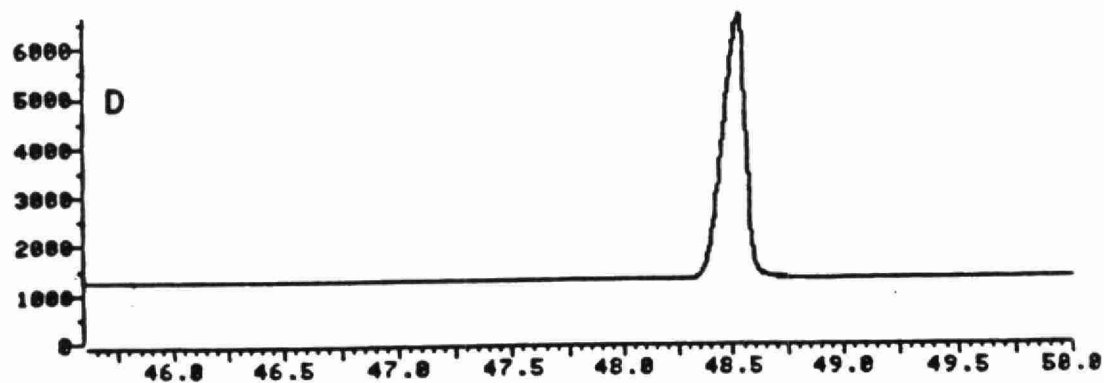
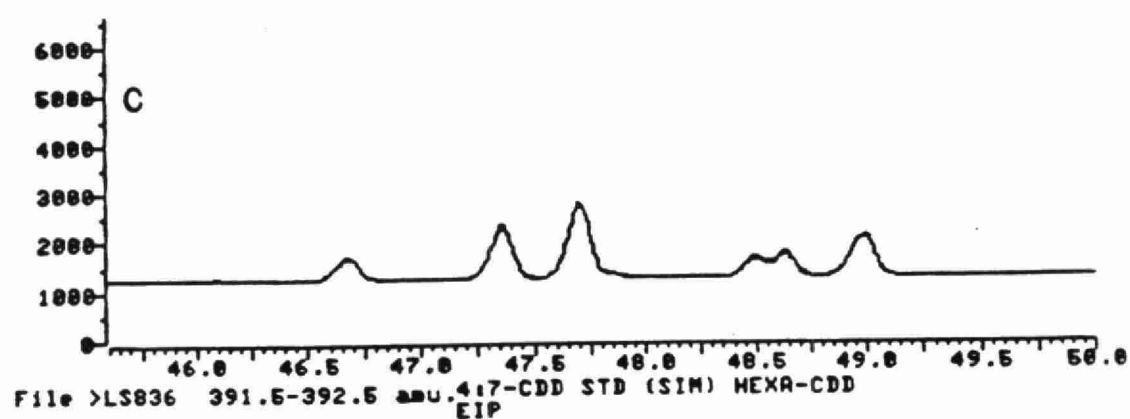
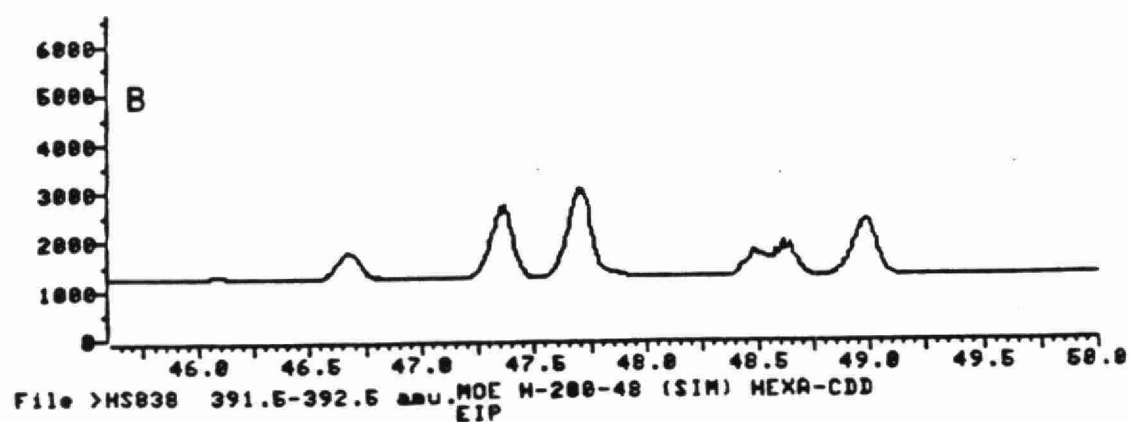
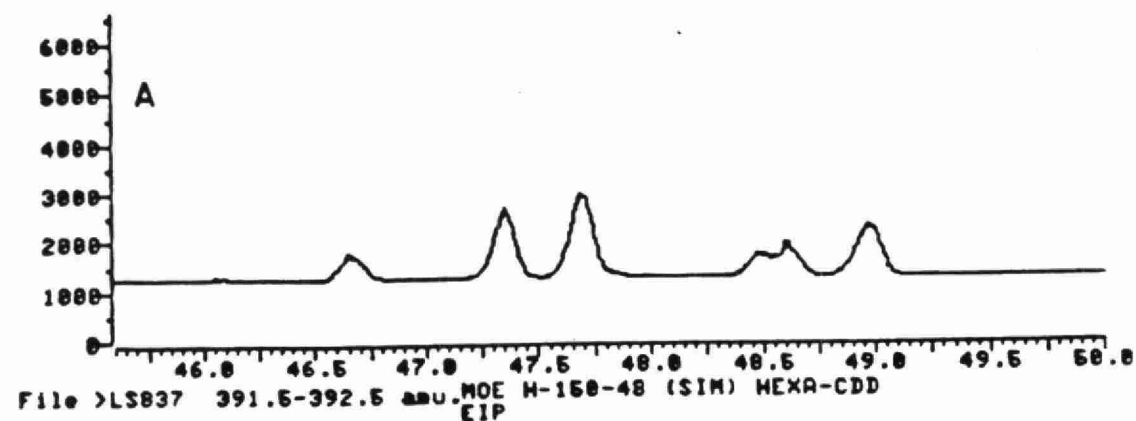
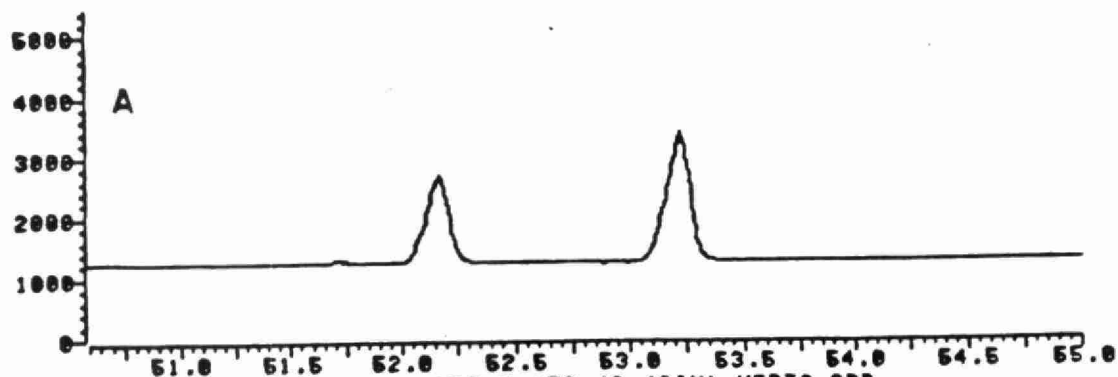
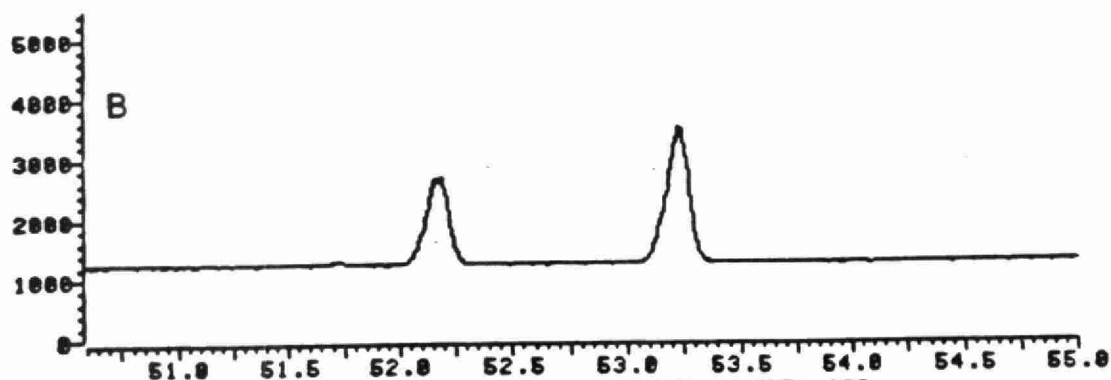


FIGURE 8 GC-MS-SIM ANALYSES FROM TIME AND TEMPERATURE STUDY H7CDD

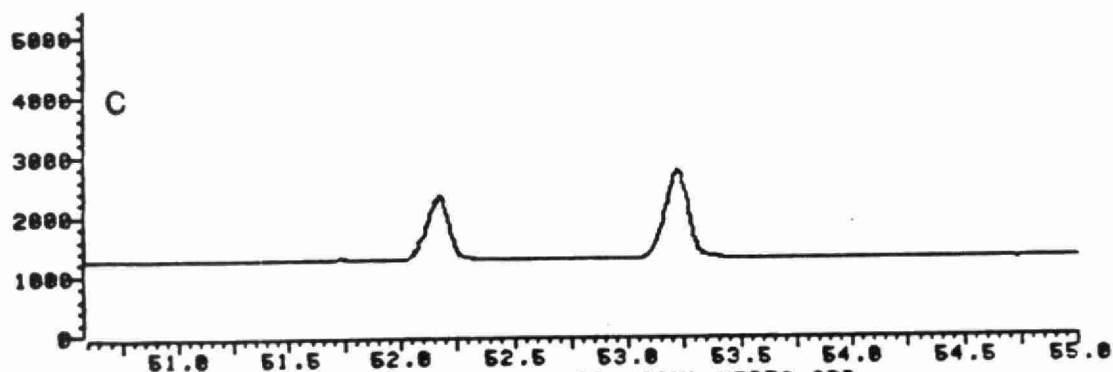
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EIP



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EIP



File >HS838 425.5-426.5 amu.MOE H-200-48 (SIM) HEPTA-CDD
EIP



File >LS836 425.5-426.5 amu.417-CDD STD (SIM) HEPTA-CDD
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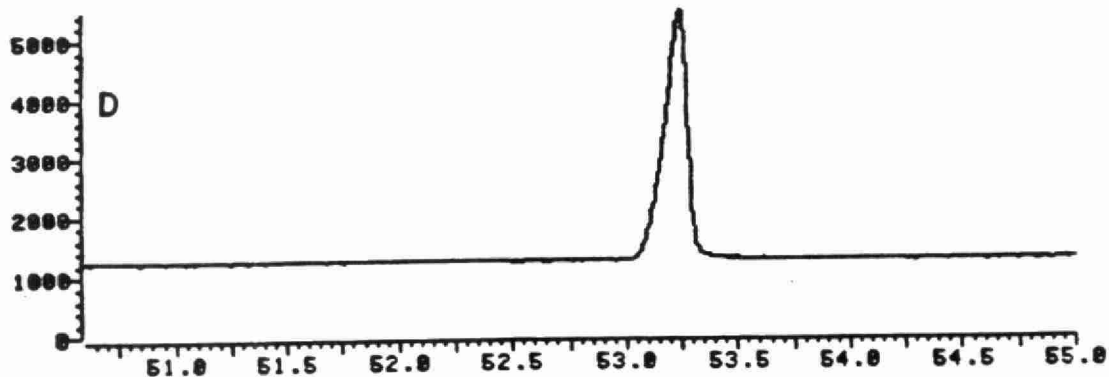
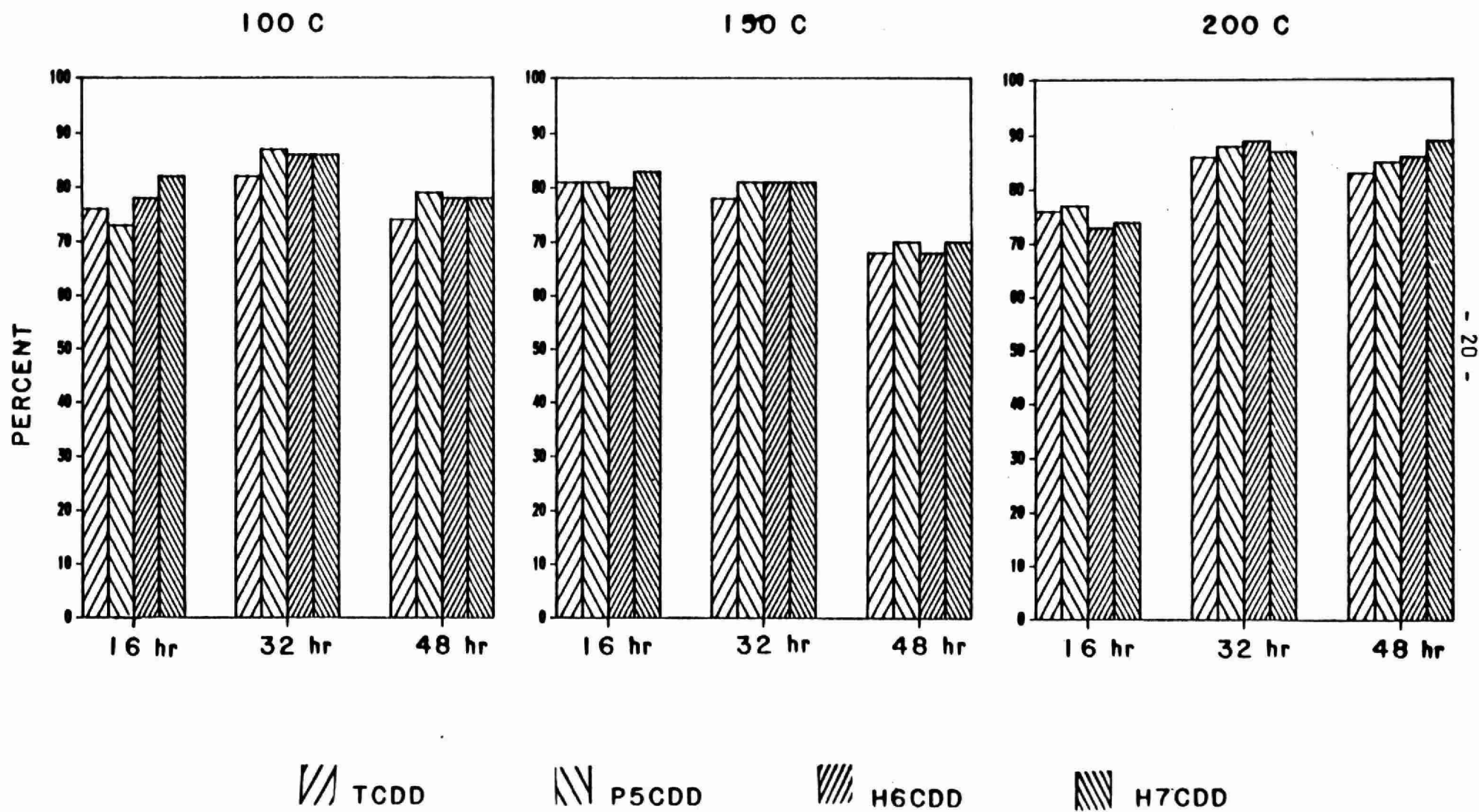


TABLE 3: Percent of Dioxins Lost due to Heating
Time and Temperature Study

Time	100°C			150°C			200°C		
	16h	32h	48h	16h	32h	48h	16h	32h	48h
<u>Dioxin</u>									
TCDD	76 ^a	82	74	81	78	68	76	86	83
P ₅ CDD	73	87	79	81	81	70	77	88	85
H ₆ CDD	78	86	78	80	81	68	73	89	86
H ₇ CDD	82	86	78	83	81	70	74	87	89

^a Percentage of Original Amount

FIGURE 9 PERCENT PCDD LOST BY DESORPTION AT 100 mL/min N₂
TIME AND TEMPERATURE STUDY



2,3,7,8-TCDD to be $3.9 - 15.9 \times 10^{-2}$ Pa at 100°C and found its decomposition temperature in nitrogen to be between 850 and 1100°C . If this model is correct, the apparent rate of desorption (ng/g/hr/L) would have a finite value at the start of heating and would approach zero as the amount of physisorbed material approached zero. An illustration of this proposed model is shown in Figure 10.

Time Study at Constant Temperatures

Since the desorption behaviour was unknown, the initial experiments were conducted under high temperature, time and flow conditions. After obtaining positive results there, the next step was to obtain data under conditions nearer to those in stack sampling.

Figure 11 shows the analysis of the labelled internal standards, dissolved in benzene. The plots show that there are no ions in the labelled analogues of the dioxins which would interfere with the quantitation of the unlabelled forms. Under this condition the molar ratio of the analyte to the internal standard is the ratio of the areas of the analyte and the internal standard (13).

The percent loss of PCDD at 120°C after heating at 2, 4, and 6 hours in a 100 ml/min stream of dry nitrogen is presented in Table 4 and shown in Figure 12. There are no apparent differences in PCDD lost after heating for 2 and 4 hours, which may be due to the relative errors of the analyses, which vary from 0.11 to 0.40.

These data, as illustrated in Figure 12 possess an interesting feature. The percent loss of PCDD due to heating decreases in order of TCDD, H_6CDD , P_5CDD , H_7CDD . If the desorption of physisorbed material is governed solely by vapour pressure, the order would be expected to be that of increasing molar mass i.e. TCDD, P_5CDD , H_6CDD , H_7CDD . The switching of the order for P_5CDD and H_6CDD

FIGURE 10 PROPOSED MODEL OF PCDD DESORPTION FROM FLYASH

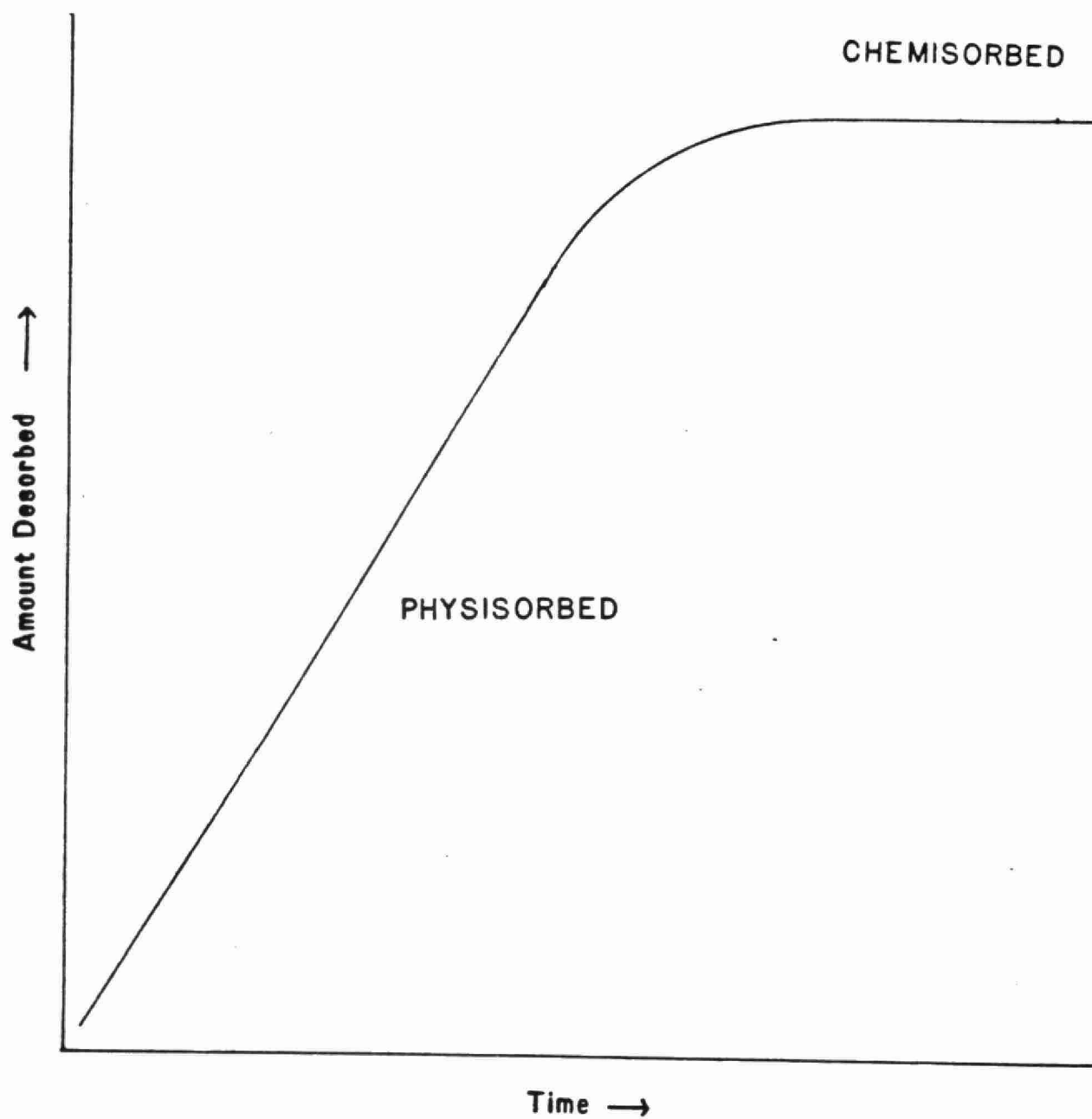


FIGURE 11 GC-MS-SIM ANALYSIS OF INTERNAL STANDARDS

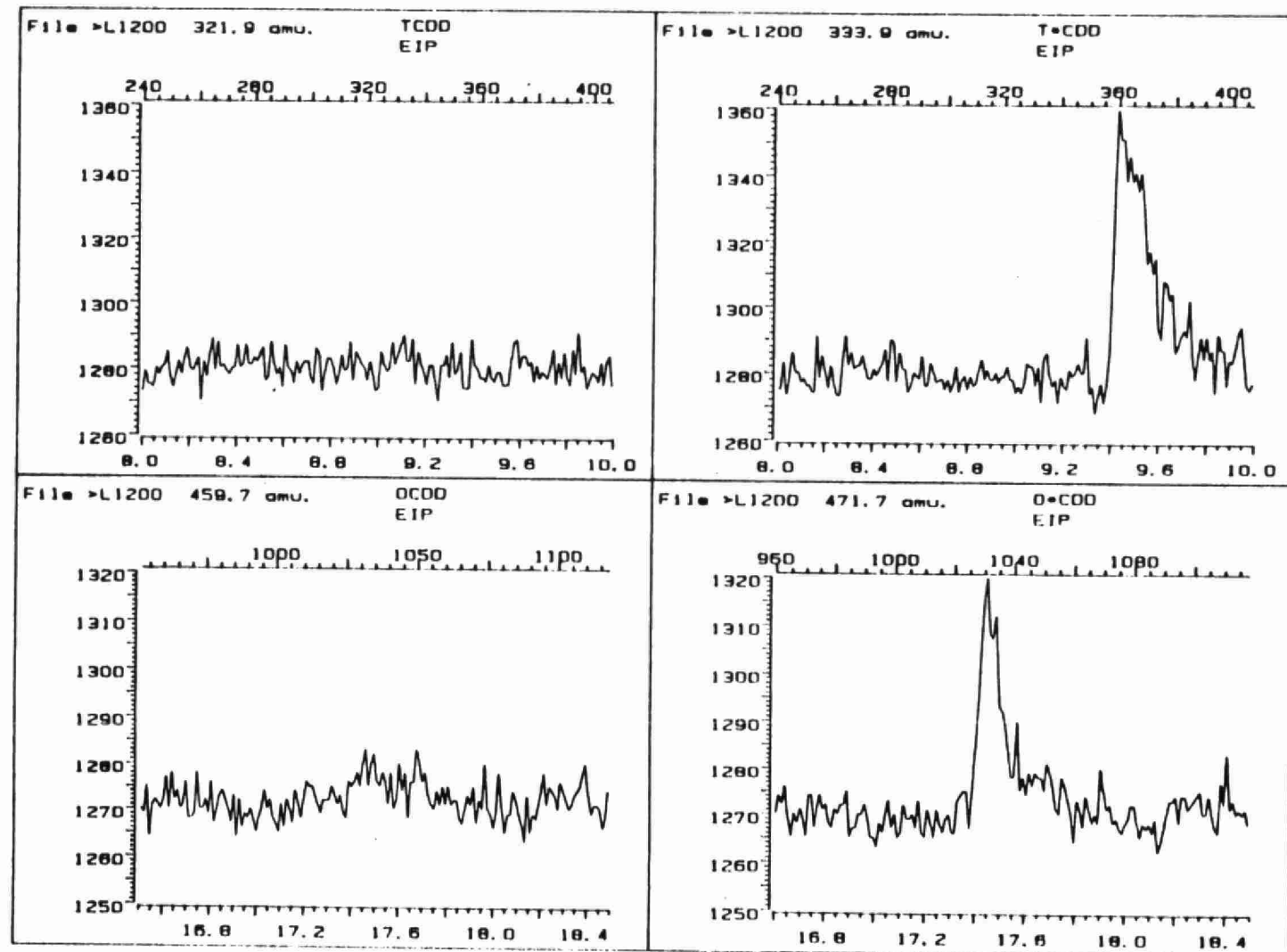


TABLE 4: Dioxins Desorbed due to Heating Time
Study at Constant Temperature

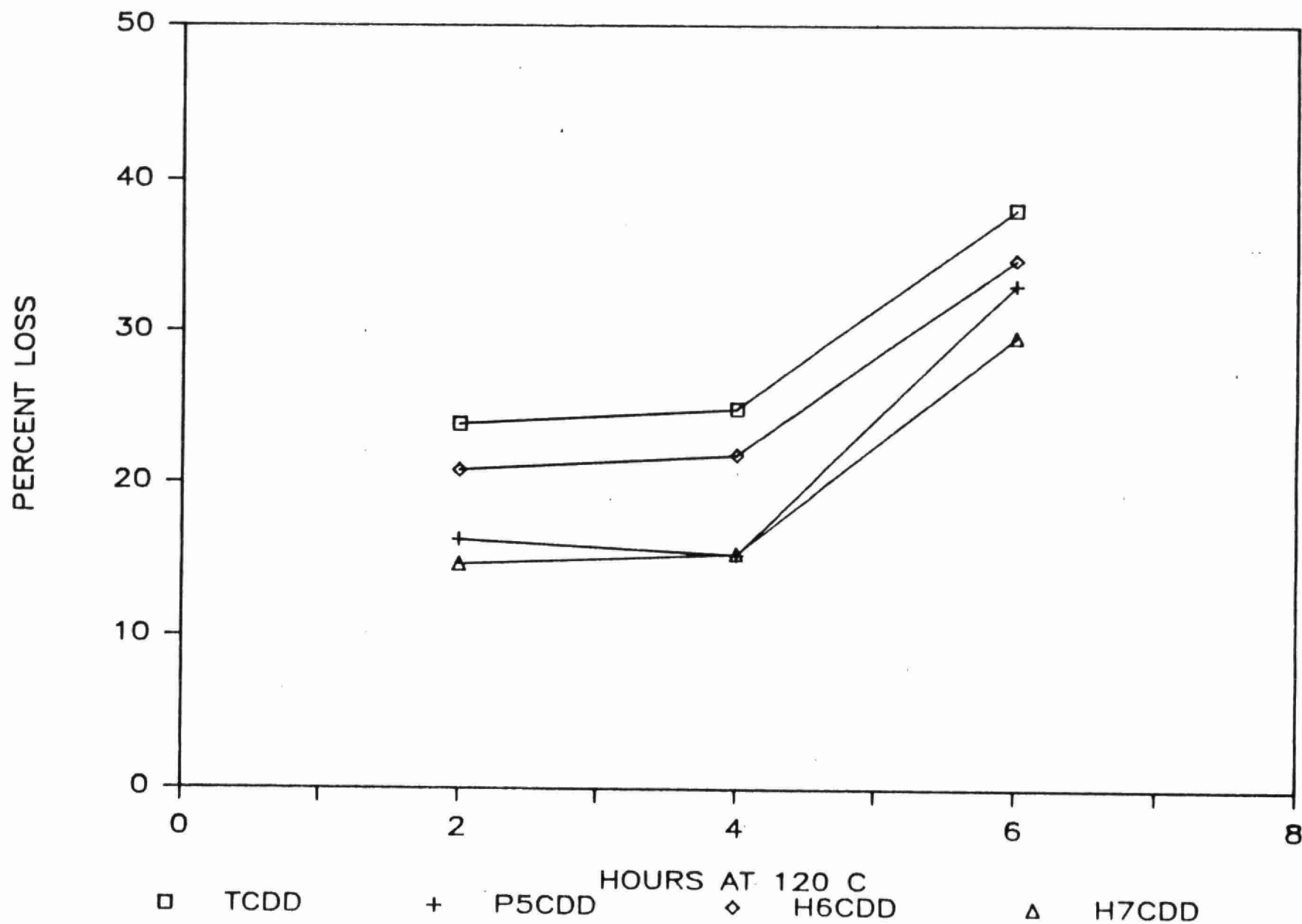
Dioxin Loss (Percent of Original Amount)

Time	TCDD	P ₅ CDD	H ₆ CDD	H ₇ CDD
2h	24 ± 6 ^a	16 ± 5	21 ± 4	15 ± 6
4h	25 ± 6	15 ± 5	22 ± 4	15 ± 6
6h	38 ± 6	33 ± 5	35 ± 4	20 ± 6

^aStandard Error of the Mean estimated from error mean square of analysis of variance, 2 replicates per sample.

FIGURE 12

HEAT DESORPTION OF PCDD
TIME STUDY AT CONSTANT TEMPERATURE



could be due to dipolar interactions. Both TCDD and H₆CDD congener classes possess an even number of chlorine and hydrogen atoms and can form structures which possess no net dipole moment. Conversely, P₅CDD and H₇CDD have odd numbers of chlorine and hydrogen atoms and therefore are unable to form structures without a net dipole moment. We speculate that an increased average level of the van der Waals forces between the molecules results in greater retention of P₅CDD and H₇CDD congener classes. More exact and precise desorption data for each congener class is needed before any reliable conclusions can be reached.

A plot of desorption data taken from both studies is presented in Figure 13. The three sets of points below 10 minutes, shown as circles, are taken from the time study at 120°C while points shown by squares are from the time and temperature study. The latter data are averages of data taken at the three temperatures. The data for 48 hours is omitted for clarity. The plot resembles the proposed model for PCDD desorption presented in Figure 10. The rising portion of the desorption curve represents the loss of physisorbed material from the flyash. The plateau of the curve for heating times greater than 16 hours represents the retention of material chemisorbed onto the surface of the flyash particles.

Desorption rates for PCDD have been estimated from data taken from both studies. Table 5 presents the PCDD loss data (ng/g) used to calculate desorption rates (ng/g hr/L). The data from the 2 hour experiments was suspect and therefore omitted. The calculated desorption rates for each congener class are presented in Table 6 and illustrated in Figure 14. The best-fitting line was calculated using linear regression techniques. The desorption rates increase from TCDD to H₇CDD. This increase is more likely due to the relative amounts of each congener found on flyash than an effect of increasing molar mass. The values listed under intercept do not have any physical meaning as no PCDD would be desorbed in 0 hours.

FIGURE 13

HEAT DESORPTION OF PCDD
COMBINED STUDIES

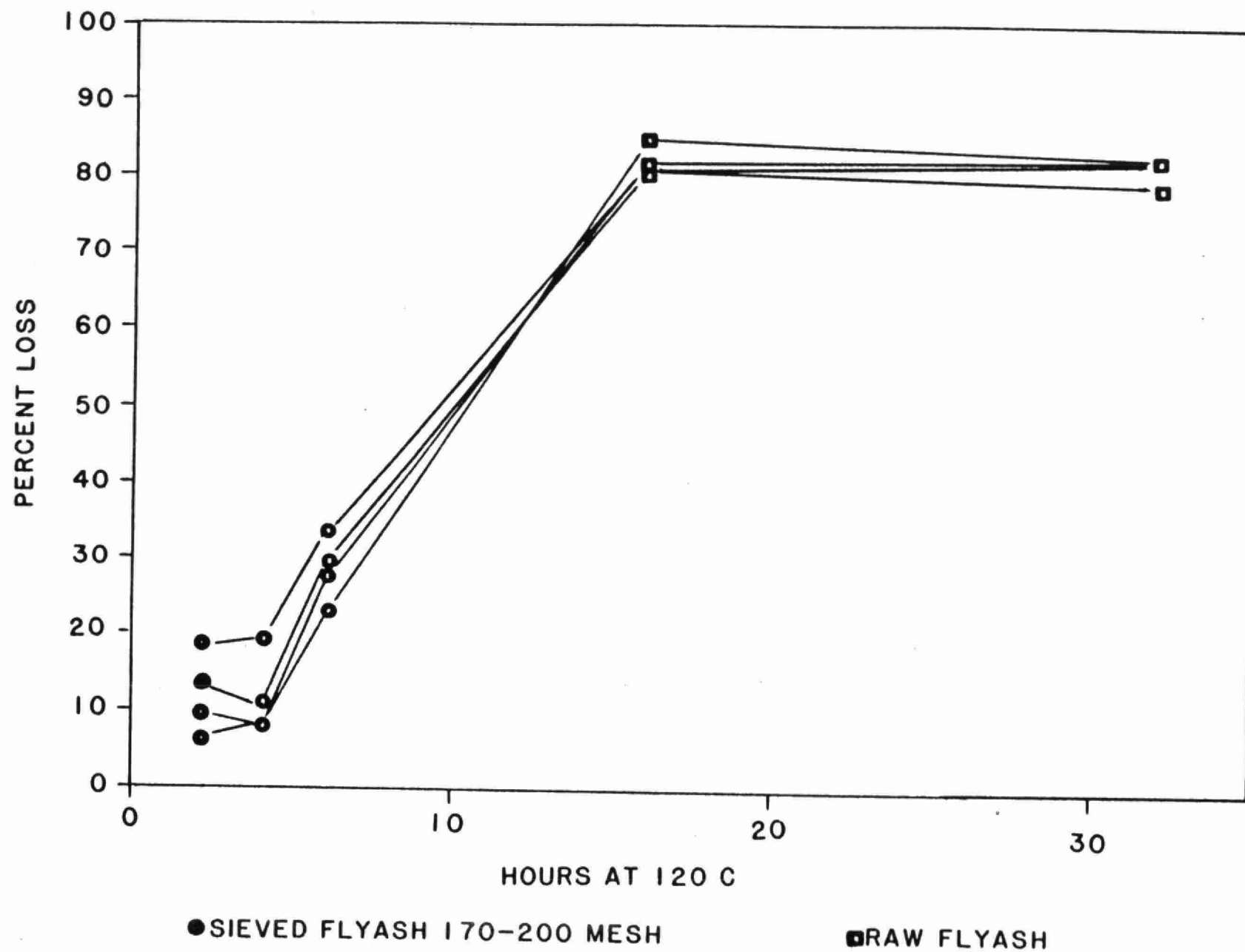


TABLE 5: Dioxins Desorbed due to Heating
Selected Data from Both Studies

<u>Dioxin Loss (ng/g)</u>				
Time	TCDD	P ₅ CDD	H ₆ CDD	H ₇ CDD
4h	1.5	1.4	4.5	4.3
	1.2	2.0	4.2	3.9
6h	2.2	3.8	7.2	7.5
	1.9	3.4	6.6	8.1
16h	4.0 ^a	7.8	15.5	21.5
	4.3	8.7	15.9	22.0
	4.0	8.3	14.4	19.4

^aData from Time and Temperature Study are averages of the losses at the three temperatures at N₂ flow of 6 L/min.

TABLE 6: Desorption Rate of Dioxins^a

Dioxin	Desorption Rate (ng/g/hr/L)	Slope (ng/g/hr)	Intercept
TCDD	$0.0368 \pm .006^b$	$0.221^c \pm .037^d$	0.584
P ₅ CDD	0.0865 ± 0.016	$0.519 \pm .094$	0.016
H ₆ CDD	0.147 ± 0.019	$0.884 \pm .113$	1.169
H ₇ CDD	0.229 ± 0.020	$1.374 \pm .177$	-0.965

^aData taken from Table 5

^b95% confidence interval for desorption rate

^cslope of corresponding best-fitting line in Figure 13.

^d95% confidence interval for slope

FIGURE 14 PCDD DESORPTION RATES (ng/g/hr)
COMBINED STUDIES

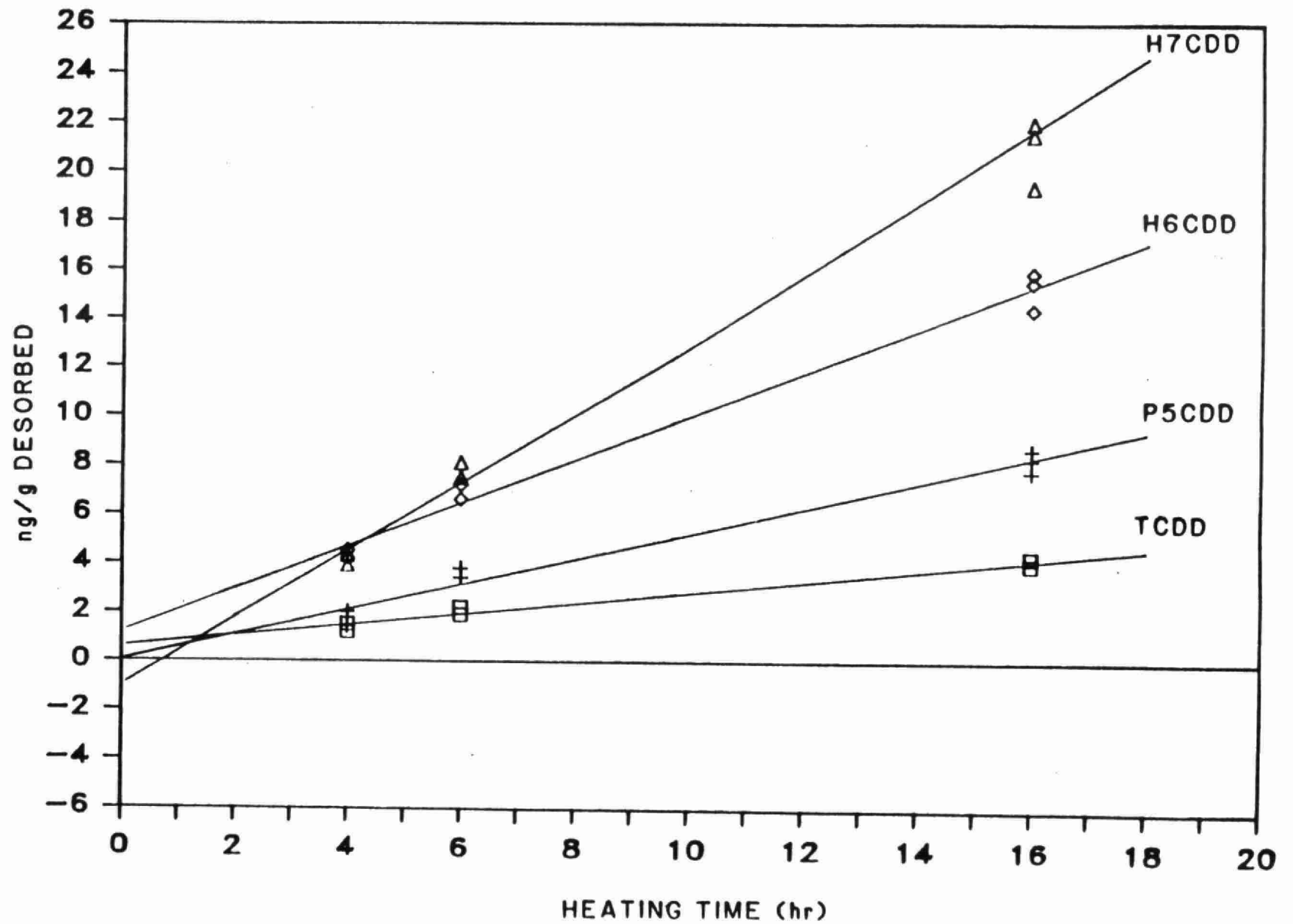


Table 7 presents desorption data, expressed as percentages of the original amount on the flyash. The data selected corresponds to the desorption data presented in Table 5. These data were used to calculate desorption rates, expressed as percent/hr/L, and are shown in Table 8. The desorption rates for the congeners are equal, within experimental error. Therefore, the data for the four congener classes were combined and a desorption rate based on the combined data was calculated. These data and the best-fitting line are presented in Figure 15. These data show that desorption rates in percent/hr/L are equal for each congener. This confirms our speculation that desorption rates expressed as ng/g/hr/L are more dependent upon the amount of physisorbed material in the flyash than on the molar mass of the material.

Table 9 shows the amount of PCDD found on the trap flyash just downstream of the desorbed flyash. The listed values are from single analyses so the variances are high. The apparent trend follows the desorption data, with increasingly larger amounts recovered with an increasingly larger amount desorbed.

Table 10 compares the amount desorbed to the amount absorbed on unextracted flyash. These data indicate that the PCDD were desorbed from flyash and reabsorbed downstream without significant decomposition. It is far more difficult to obtain reliable adsorption data than to obtain desorption data due to condensation of PCDD on the surface of the flow tube and absorption by the glass frit. Further experiments must be carefully designed before useful adsorption data can be produced.

TABLE 7: Dioxins Desorbed due to Heating
Selected Data from both Studies

Dioxin Loss (Percentage of Original Amount)

Time	TCDD	P ₅ CDD	H ₆ CDD	H ₇ CDD
4 hr	28	13	23	16
	23	19	21	15
6 hr	42	35	36	29
	36	32	33	31
16 hr	76 ^a	73	78	82
	81	81	80	84
	76	77	73	74

^a Data from Time and Temperature Study are averages of the losses at the three temperatures.

TABLE 8: Desorption Rate of Dioxins^a

Dioxin	Desorption Rate (percent/hr/L)	Slope (percent/hr)	Intercept
TCDD	$0.694^b \pm .112^c$	$4.164^b \pm .673^d$	11.01
P ₅ CDD	$0.803^b \pm .146$	$4.815 \pm .873$	0.114
H ₆ CDD	$0.745^b \pm .093$	$4.471 \pm .556$	5.86
H ₇ CDD	$0.870^b \pm .112$	$5.217 \pm .669$	-3.65
Combined	$0.778^e \pm .067$	$4.667 \pm .404$	3.33

^a Data taken from Table 7

^b 7 data points

^c 95% confidence interval for desorption rate

^d 95% confidence interval for slope

^e 28 data points

FIGURE 15 PCDD DESORPTION RATE (%/hr)
COMBINED STUDIES

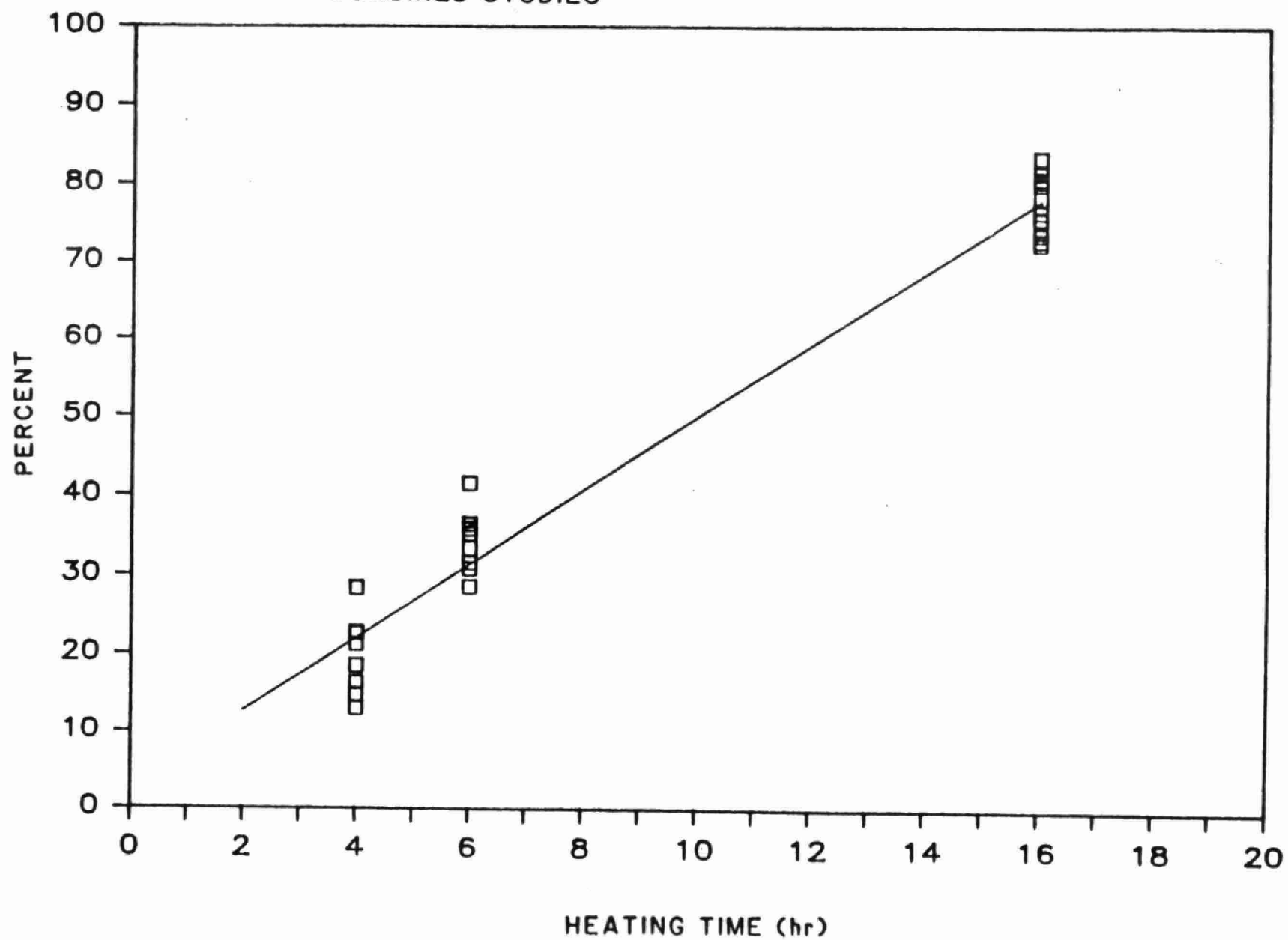


TABLE 9: Amount of Dioxins on Trap Flyash Dioxin (ng/g)^a

Time	TCDD	P ₅ CDD	H ₆ CDD	H ₇ CDD
2 hr	ND ^b	ND	ND	6
4 hr	2	3	5	8
6 hr	2	4	8	11

^a OCDD not quantitated

^b Not detected

TABLE 10: Amount of Dioxins Desorbed Compared to Amount of Dioxins Absorbed on Unextracted Flyash

Time -----	TCDD -----		P ₅ CDD -----		H ₆ CDD -----		H ₇ CDD -----	
	Loss	Trap	Loss	Trap	Loss	Trap	Loss	Trap
2 hr	18 ^a	ND ^b	26	ND	61	ND	56	75
4 hr	15	25	22	29	56	48	51	76
6 hr	31	26	55	52	106	104	118	143

^ang dioxin

^bnot detected

Recommendations

The precision of the analyses needs to be improved to allow more precise determinations of desorption rates. Variables which affect desorption should be identified and closely controlled. These factors could include temperature, nature of the gas, gas flow rate, particle size and particle packing.

The absorption behaviour of PCDD on fluorisil should be compared to flyash, since fluorisil is used as the absorbant in the sampling train.

The desorption apparatus should be redesigned to give reliable absorption data. Care should be taken to reduce condensation of material on the apparatus walls.

The desorption behaviour of PCDD may be different in the presence of moisture and oxygen found in air than that in dry nitrogen. It is possible that surface-catalyzed reactions of PCDD with oxygen and/or moisture may occur. Therefore to better approximate conditions in the sampling train, standard grades of compressed air should be used in further desorption studies. Other gases could also be added to closely approximate actual stack conditions.

The gas flow through the tube should be increased to 0.75 cfm as per stack sampling conditions.

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